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MANGANESE DRY CELL

[マンガン電池]

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[Scope of Patent Claims]

[Claim 1] A manganese dry cell using an anode made of a zinc alloy, characterized in that said zinc alloy does not contain lead nor cadmium but contains 30 to 8,000 ppm of bismuth and 10 to 1,000 ppm of one type or two or more types of alkali earth metals (Mg, Ca, Sr, Ba) relative to the weight of zinc.

[Detailed Description of the Invention]

[0001]

[Field of the Invention] The present invention relates to a manganese dry cell, which uses an anode made from a zinc alloy.

[0002]

[Prior Art] Figure 1 shows the structure of a manganese dry cell. In Figure 1, (1) represents zinc (anode), (2) represents a separator, (3) represents a cathode mix, (4) represents a carbon rod, (5) represents a sealing body, (6) represents a cathode terminal plate, (7) represents an anode terminal plate, (8) represents an insulating tube and (9) represents a packaging can. As the anode of a manganese cell, a zinc can (hereinafter, called "anode can"), which is also used as the container, is conventionally used. As the material of said zinc can, a zinc alloy, which contains 200 to 600 ppm of cadmium and more than 50 ppm of lead, is used to add a stretching property

¹Numbers in the margin indicate pagination in the foreign text.

and mechanical strength, which are required in the can manufacturing process, and give corrosion resistance to the electrolytic solution, which is the content of said anode can.

[0003] However, even minute amounts of cadmium and lead, which are contained in said zinc alloy, are harmful to the human body and, as the amount of consumption is increased, they are mixed in industrial waste or household waste thereby becoming the substances responsible for environmental pollution. Currently, it becomes imperative to prevent the above described environmental pollution. It is strongly hoped that, as the countermeasure, a zinc alloy, which does not contain cadmium and lead, is used as the material for the anode can of a manganese dry cell.

[0004]

[Problem to Be Solved by the Invention] However, the zinc alloy, which is made by simply removing cadmium from a conventionally-used zinc alloy, has extremely low mechanical strength compared with the zinc alloy, which contains cadmium, and generates imperfection or deformation during the process of manufacturing the dry cell thereby causing internal short circuit. In addition, the zinc alloy, which is made by simply removing lead from a conventionally-used zinc alloy, is easily corroded by the electrolytic solution within the cell compared with the zinc alloy, which contains lead, thereby significantly decreasing the long-term storage performance.

[0005] The present invention was created to solve the above described problem. The objective of the present invention is to provide a manganese dry cell, which uses an anode made from a zinc alloy, wherein said zinc alloy does not contain cadmium and lead, but has the same mechanical strength and corrosion resistance as those of the conventional anode can.

[0006]

[Means to Solve the Problem] To achieve the above described objective, the manganese dry cell, according to the present invention, is characterized in that the zinc alloy, which is used as the anode, contains 30 to 8,000 ppm of bismuth and 10 to 1,000 ppm of one type or two or more types of alkali earth metals (Mg, Ca, Sr, Ba) relative to the weight of zinc.

[0007]

[Operation] Bismuth, which is used as one of the elements of the zinc alloy, adds corrosion resistance to the zinc alloy. When the amount of bismuth is less than 30 ppm, despite its small effect, it is not possible to obtain sufficient corrosion resistance. When the amount of bismuth is more than 8,000 ppm, despite its effect of suppressing the corrosion, it is not possible to obtain the significant effect considering its amount and the cost is rather increased, which is not desirable. The mechanism, wherein the corrosion resistance of the zinc alloy against the electrolytic solution is improved by adding bismuth, has not yet been clarified.

[0008] In addition, according to the present invention, alkali earth metals (Mg, Ca, Sr, Ba) gives mechanical strength to the zinc alloy and, by adding bismuth, it is possible to improve the deteriorating rolling workability. When the amount of said alkali earth metals is less than 10 ppm, it is not possible to sufficiently improve the rolling workability. When the amount of the alkali earth metals is more than 1,000 ppm, the corrosion resistance of the zinc alloy becomes insufficient. Here, one type or two or more types of alkali earth metals may be used and they are effective as long as their amount does not exceed the above described range.

[0009] Here, it is inevitable that, in the purification process, impurities such as copper, iron, cadmium and lead are mixed in zinc on a ppm basis. However, according to the present invention, existence of such a small amount of inevitable impurities does not cause any problem.

[0010]

[Description of the Working Example] Next, the working examples of the present invention will be described. Zinc metal, which was electrolytically refined and had a purity of 99.99 wt. % or higher, was used. Bismuth, magnesium, calcium, strontium and barium were formulated into said zinc metal in the proportions, which are shown in Tables 1 and 2, thereby producing alloy specimens of Working Examples 1 to 96. For comparison, the conventional product containing lead and cadmium was used as Comparative Example 1 (see Table 3).

In addition, as Comparative Examples 2 to 27 (see Table 4), the zinc alloys, wherein lead and cadmium were not contained, bismuth and alkali earth metals were contained and the amount of bismuth and the alkali earth metals was above or below the range of the present invention, were used.

[0011] The above described alloys were tested and evaluated in a manner described below. Here, (n) represents the number of the specimens of each of the examples.

1) Corrosion Weight Loss (n = 3)

By using a mixture of flake graphite and boric acid as a lubricant, an anode can was made from a zinc alloy pellet, which was obtained in the rolling workability test (3) below, by impact extruding. The obtained anode can was cut into specimens with dimensions of 50 × 50 mm. The surface of each of the specimens was polished with sandpaper until it was smooth. Then, the specimens were alkali degreased, washed with water, dried and weighed. They were immersed in an electrolytic solution for the manganese dry cell, which had been preliminarily prepared and stored at constant temperature of 45°C for 100 hours. After that, the specimens were retrieved, washed with water, dried and weighed. The weight loss of each of the specimens was measured and divided by the surface area of each of the specimens thereby obtaining the corrosion weight loss (mg/cm²).

[0012] 2) Gas Yield from the Cell (n = 5)

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60 portions by weight of manganese dioxide with a purity of 70 % or higher, 10 portions by weight of acetylene black and 0.6 portion by weight of zinc oxide were thoroughly mixed. Then, 49 portions by weight of electrolytic solution having 25 wt. % of zinc chloride and 2.0 wt. % of ammonium chloride was added to said mixture and thoroughly stirred thereby formulating a homogeneous cathode mix, which was to be used as the cathode. On the other hand, the anode can, which was obtained in the corrosion weight loss test described above in 1), was used as the anode. Starch for preserving the electrolytic solution was coated on craft paper and the resultant coated paper was used as the separator. By using the above described materials, a R20-type dry cell was made. The obtained cell was placed into a graduated cylinder, which was filled with liquid paraffin, and stored at 60 °C so that the generated gas was collected in the cylinder by upward delivery. After the cell was stored for 20 days, the amount of the collected gas was measured.

[0013] 3) Rolling Workability

An alloy specimen (thickness: 20 mm; width: 100 mm; and length: 500 mm) was rolled by a heating roller press at 180 to 220°C so as to obtain a plate with the thickness of 5 mm. After the rolling process, the obtained alloy plate was punched into 20-type hexagonal pellets with a diagonal plane of 31.0 mm. The number of the obtained pellets was counted. Then, an alloy, which contained lead, was processed in the same manner as the above thereby obtaining pellets. By converting

the number of the latter pellets to 100% and comparing it with the number of the former pellets, the rolling workability (%) of the former pellets was obtained.

[0014] Here, in the case of the alloy specimen with poor rolling workability, crack or breakage was generated on both ends of the alloy plate and its surface during the rolling process, crack or breakage was generated in the punched pellets and the number of the obtained pellets, which were normal, was decreased.

[0015]

[Table 1]

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No.	Composition of the Alloy (ppm)					Corrosion Weight Loss (mg/cm ²)	Gas Yield (ml)	Rolling Workability (%)
	Bi	Mg	Ca	Sr	Ba			
1	30	10	0	0	0	4.56	170	90
2	30	0	10	0	0	4.56	171	90
3	30	0	0	10	0	4.57	170	91
4	30	0	0	0	10	4.58	172	91
5	30	100	0	0	0	4.54	168	92
6	30	0	100	0	0	4.56	171	93
7	30	0	0	100	0	4.57	171	93
8	30	0	0	0	100	4.55	170	92
9	30	500	0	0	0	4.55	169	94
10	30	0	500	0	0	4.55	170	94
11	30	0	0	500	0	4.57	172	94
12	30	0	0	0	500	4.56	172	95
13	30	1000	0	0	0	4.56	171	100
14	30	0	1000	0	0	4.57	171	100
15	30	0	0	1000	0	4.60	174	100
16	30	0	0	0	1000	4.59	173	100
17	100	10	0	0	0	3.95	157	94
18	100	0	10	0	0	3.98	158	95
19	100	0	0	10	0	4.00	160	95
20	100	0	0	0	10	3.97	157	94
21	500	100	0	0	0	3.25	150	94
22	500	0	100	0	0	3.28	153	95
23	500	0	0	100	0	3.29	155	96
24	500	0	0	0	100	3.26	150	95
25	1000	10	0	0	0	3.05	137	93
26	1000	0	10	0	0	3.08	140	94
27	1000	0	0	10	0	3.09	142	93
28	1000	0	0	0	10	3.05	138	94
29	1000	100	0	0	0	3.07	140	95
30	1000	0	100	0	0	3.09	141	96
31	1000	0	0	100	0	3.10	143	96
32	1000	0	0	0	100	3.08	140	95
33	1000	1000	0	0	0	3.06	138	100
34	1000	0	1000	0	0	3.10	142	100
35	1000	0	0	1000	0	3.11	142	100
36	1000	0	0	0	1000	3.09	141	100
37	2000	100	0	0	0	2.99	134	96
38	2000	0	100	0	0	3.01	135	96
39	2000	0	0	100	0	3.00	134	96
40	2000	0	0	0	100	3.02	136	96
41	5000	1000	0	0	0	2.97	133	100
42	5000	0	1000	0	0	2.98	134	100
43	5000	0	0	1000	0	2.99	135	100
44	5000	0	0	0	1000	2.98	134	100
45	8000	10	0	0	0	2.76	121	95
46	8000	0	10	0	0	2.76	122	96
47	8000	0	0	10	0	2.78	123	95
48	8000	0	0	0	10	2.77	122	96

[0016]

[Table 2]

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No.	Composition of the Alloy (ppm)					Corrosion Weight Loss (mg/cm ²)	Gas Yield (ml)	Rolling Workability (%)	
	Bi	Mg	Ca	Sr	Ba				
49	8000	100	0	0	0	2.75	121	96	
50	8000	0	100	0	0	2.75	129	97	
51	8000	0	0	100	0	2.77	122	97	
52	8000	0	0	0	100	2.79	123	96	
53	8000	500	0	0	0	2.75	120	98	
54	8000	0	500	0	0	2.78	122	99	
55	8000	0	0	500	0	2.79	123	98	
56	8000	0	0	0	500	2.77	123	99	
57	8000	1000	0	0	0	2.76	121	100	
58	8000	0	1000	0	0	2.77	122	100	
59	8000	0	0	1000	0	2.78	122	100	
60	8000	0	0	0	1000	2.79	121	100	
61	30	10	10	0	0	4.55	170	95	
62	30	500	500	0	0	4.57	172	100	
63	30	10	0	10	0	4.56	171	96	
64	30	500	0	500	0	4.57	172	100	
65	30	10	0	0	10	4.56	171	96	
66	30	500	0	0	500	4.57	171	100	
67	30	0	10	10	0	4.58	172	96	
68	30	0	500	500	0	4.59	173	100	
69	30	0	10	0	10	4.56	171	96	
70	30	0	500	0	500	4.58	172	100	
71	30	0	0	10	10	4.59	173	96	
72	30	0	0	500	500	4.58	172	100	
73	1000	100	100	0	0	3.04	136	96	
74	1000	100	0	100	0	3.05	136	97	
75	1000	100	0	0	100	3.04	135	96	
76	1000	0	100	100	0	3.06	137	97	
77	1000	0	100	0	100	3.06	138	98	
78	1000	0	0	100	100	3.07	138	99	
79	5000	500	500	0	0	2.98	132	100	
80	5000	500	0	500	0	2.98	132	100	
81	5000	500	0	0	500	2.97	133	100	
82	5000	0	500	500	0	2.98	134	100	
83	5000	0	500	0	500	2.97	133	100	
84	5000	0	0	500	500	2.97	133	100	
85	8000	100	100	0	0	2.74	119	99	
86	8000	500	500	0	0	2.75	120	100	
87	8000	100	0	100	0	2.76	121	99	
88	8000	500	0	500	0	2.75	120	100	
89	8000	100	0	0	100	2.75	121	99	
90	8000	500	0	0	500	2.76	121	100	
91	8000	0	100	100	0	2.76	122	99	
92	8000	0	500	500	0	2.77	122	100	
93	8000	0	100	0	100	2.77	122	99	
94	8000	0	500	0	500	2.78	123	100	
95	8000	0	0	100	100	2.76	122	99	
96	8000	0	0	500	500	2.77	123	100	

[0017]

[Table 3]

No.	Composition of the Alloy (ppm)		Corrosion Weight Loss (mg/cm ²)	Gas Yield (ml)	Rolling Workability (%)
	Pb	Cd			
1	1600	400	4.68	181	100

[0018]

[Table 4]

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No.	Composition of the Alloy (ppm)					Corrosion Weight Loss (mg/cm ²)	Gas Yield (ml)	Rolling Workability (%)
	Bi	Mg	Ca	Sr	Ba			
2	10	0	0	0	0	4.51	185	48
3	30	0	0	0	0	4.52	186	51
4	30	5	0	0	0	4.54	188	63
5	30	0	5	0	0	4.55	189	63
6	30	0	0	5	0	4.54	188	62
7	30	0	0	0	5	4.55	189	62
8	30	2000	0	0	0	4.86	185	100
9	30	0	2000	0	0	4.89	188	100
10	30	0	0	2000	0	4.87	186	100
11	30	0	0	0	2000	4.90	189	100
12	8000	0	0	0	0	2.73	118	65
13	8000	5	0	0	0	2.76	121	71
14	8000	0	5	0	0	2.76	121	71
15	8000	0	0	5	0	2.77	122	70
16	8000	0	0	0	5	2.76	122	70
17	8000	2000	0	0	0	3.25	150	100
18	8000	0	2000	0	0	3.26	150	100
19	8000	0	0	2000	0	3.28	152	100
20	8000	0	0	0	2000	3.27	151	100
21	8000	1000	1000	0	0	3.28	151	100
22	8000	1000	0	1000	0	3.29	152	100
23	8000	1000	0	0	1000	3.28	150	100
24	8000	0	1000	1000	0	3.27	153	100
25	8000	0	1000	0	1000	3.27	151	100
26	8000	0	0	1000	1000	3.29	155	100
27	10000	0	0	0	0	2.85	110	73

[0019] As is obvious from these tables, it was found that, in the case of the zinc alloy, which did not contain cadmium and lead, as the concentration of bismuth was increased, corrosion of the zinc

alloy was significantly suppressed. In addition, it was found that, when the total amount of magnesium, calcium, strontium and barium was 10 to 1,000 ppm, no problem was found with the rolling workability.

[0020] As a result, it was found that, by adding 30 to 8,000 ppm of bismuth and 10 to 1,000 ppm of alkali earth metals to the zinc alloy, which did not contain cadmium and lead, it was possible to obtain good corrosion resistance and rolling workability.

[0021]

[Effect of the Invention] As described above, according to the present invention, it is possible to obtain an anode zinc alloy, which does not contain cadmium and lead, but has good corrosion resistance and rolling workability, and thus provide a low-pollution manganese dry cell.

[Brief Description of the Drawing]

[Figure 1] Figure 1 is a longitudinal cross-sectional view of a manganese dry cell.

[Description of the Notations]

1: Zinc (Anode)

2: Separator

3: Cathode Mix

4: Carbon Rod

5: Sealing Body

6: Cathode Terminal Plate

7: Anode Terminal Plate

8: Insulating Tube

9: Packaging Can

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[Figure 1]

